

Synthesis and Characterization of Polypyrrole (PPY) Thin Film by Spin Coating Technique

S. Sakthivel and A. Boopathi

Thin film Physics and Nano Science Laboratory,
PG and Research Department of Physics
Rajah Serfoji Govt. College,
Thanjavur, Tamilnadu, INDIA.

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ABSTRACT

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer Pyrrole and ammonium per sulphate as an oxidant in a ratio of 1:1. Thin films of polypyrrole were prepared by dissolving polypyrrole in m-cresol and cast using spin coating technique on glass substrates. Thin films of polypyrrole were characterized by X ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra red spectroscopy (FTIR), UV visible spectroscopy, Raman spectroscopy and electrical resistivity measurements by four probe method.

Keywords: Polypyrrole, Chemical Polymerization, FTIR, SEM, XRD, Raman Spectrum.

1. INTRODUCTION

Conducting Polymers with conjugated double bonds have been attracted much attention as advanced materials. Polypyrrole (PPy) has received widespread interest due to its good Environmental stability, facile synthesis, and higher conductivity than many other conducting polymers^{1,2}. It could be always used in Drug

delivery systems, Rechargeable batteries, Super capacitors, Sensors, and Microwave shielding³⁻⁶. Polypyrrole (PPy) based polymer blends can protect the corrosion of metals⁷. Because of the strong adhesion of PPy to iron or steel treated with nitric acid, PPy polymers can be used as good adhesives⁸. Polypyrrole as a neural switch may be used to control and modulate the communication between different artificial

neurons⁹. Electrochemical process parameters affecting the properties of the PPy coatings are also investigated¹⁰. PPy can be easily prepared by either a chemical oxidatively or electrochemical polymerization of Pyrrole monomer. However synthetically conductive PPy is insoluble and infusible which restricts in its processing and applications of other fields. The problem has been extensively investigated and new application fields have also been explored in the past several years. For example, PPy-based polymers can be used to load and release drugs and bio molecules¹¹. PPy-based polymer blends can protect the corrosion of metals¹². In the present investigations attempts were made to report on our observation of structure morphology, optical and electrical properties of polypyrrole thin films using the spin coating technique.

2. EXPERIMENTAL

2.1 Materials

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer Pyrrole were purchased from Sigma-Aldrich (C_4H_5N , M.W. 67.09) reagent grade was distilled prior to use. Analytical grade ammonium per-sulphate APS ($(NH_4)_2S_2O_8$ M=228.20g/mol) Merck Specialities Mumbai was used as oxidizing agent. All reactions were conducted at room temperature. The solution of the oxidizing agent, APS was prepared using distilled water and used in the ratio of 1:1(monomer: oxidant). The Solvent m-cresols (C_7H_8O , M.W.108.14) were purchased from Sisco Research Laboratories Mumbai.

2.2 Preparation of Polypyrrole Thin Film

The Polypyrrole was prepared by Chemical polymerization method. 1M Pyrrole solution was prepared using distilled water and then mixed with an oxidizing agents in the ratio of 1:1, slowly under constant stirring for 30 minutes. Then the polymerization was conducted for 5 hours under constant stirring. This preparation was kept unagitated for 24 hours so polypyrrole powder settled down. Then the PPy powder was filtered out and washed with distilled water in several times to remove any impurities and reacting monomers. The Polypyrrole was dried for two days at room temperature.

The Thin film of polypyrrole was deposited using spin coating method on pre cleaned glass substrate. The polypyrrole powder was dissolved in m- cresol to prepare the concentrated solution. The solution preparation required 4-5 days of stirring make the solution homogenous. A thin film of Polypyrrole was deposited on glass substrates using spin coating technique at a speed of 3000 rpm. The thin film was dried in air at 60min.

2.3 Testing and Characterizations

FTIR and XRD analysis were used to confirm the formation of PPy powder sample. The chemical bonding was analyzed by using FTIR – Perkin Elmer make-model Spectrum RXI spectroscopy. UV-Visible measurements were carried out on Perkin Elmer make-Lambda 35 model and absorption spectra were obtained by depositing the film PPy on glass substrate. X-ray diffraction (XRD) studies were

carried out using Rigaku X-ray Diffractometer. Raman spectroscopic studied by Raman Systems RSIQ model. And Scanning Electron Microscope (SEM) studied by SEM TESCAN Vega-3 SBU model using acceleration voltage of 5.0 kV. The thin film resistance was measured by using four-point probe method.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy Analysis

The FTIR spectra of PPy powder are represented in **Figure 1**. The stretching peaks of C-N were detected at 1473 cm^{-1} . The absorption peak at 1046 cm^{-1} is corresponded to C-H and N-H deformations. The occurrence of small peaks at all these peaks is the main characteristic of PPy¹³⁻¹⁵. The peak 916.59 cm^{-1} is out of plane deformation and the small peak 792 cm^{-1} is out of plane ring deformation another one small peak of 678 cm^{-1} is C-C out of plane ring deformation or C-H rocking¹⁶.

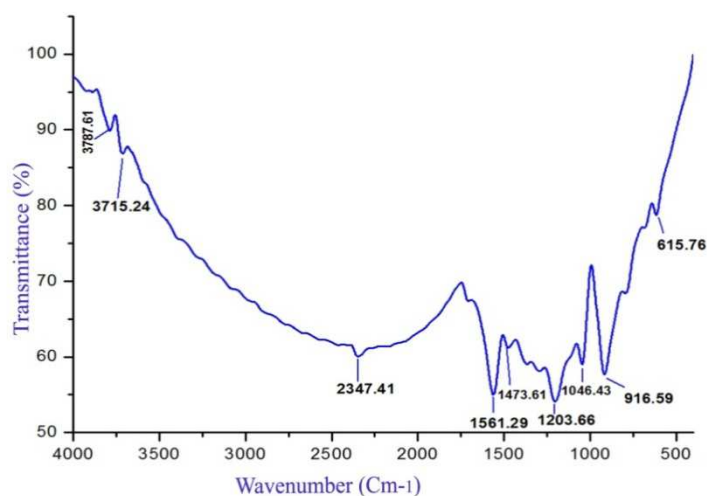


Figure1. FT-IR Spectrum of PPy Powder

3.2. X-Ray Diffraction Analysis

The X-ray diffraction (XRD) studies of the samples were done on Rigaku X-ray Diffractometer with Cu – K α radiation operating at 40kV and 15 mA. Scanning was carried out in the 2θ range from 10° to 90° at a scan speed of 10° per minute. The XRD patterns of the PPy powder are shown in **Figure 2**. The peak in PPy powder sample is

mostly amorphous in nature. Broad peak was observed at about $2\theta = 25^\circ$. The broad peak is characteristic of amorphous and indicates short range arrangement chains of PPy [17]. The crystallite size from a sharp peak at 25° for PPy is estimated by using scherrer's formula leads to the crystallite size high intensity sharp peak of about **77.412nm** for PPy powder. The value of d-spacing for PPy powder **3.5569Å**.

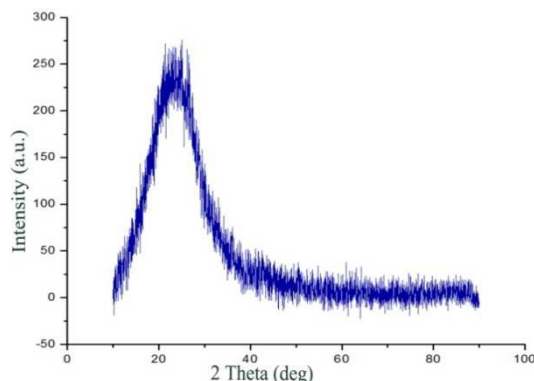


Figure 2. XRD Pattern of PPy powder

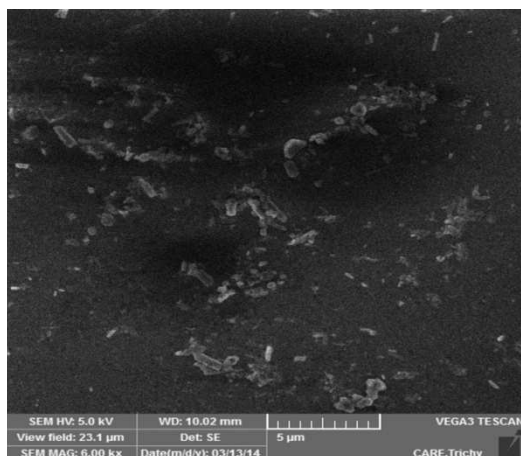


Figure 3 Scanning Electron Microscope image of PPy Thin film.

3.3 Scanning Electron Microscopy Analysis

The SEM study of PPy films shows **Figure 3** demonstrated that the surface was covered with grains. The scanning electron microscopy shows the non uniform distribution of PPy particles over the surface of substrate. The rod and spherical shape particle formation and much weaker inter-particle bonding appear to be a prominent

feature of this filling level, which may have an adverse effect on the electrical conductivity.

3.4. Raman spectral Analysis

Raman spectroscopic study is one of the important tools to obtain structural information on polymers. In most cases, Raman scattering is sensitive to the degree of crystallinity in a sample. Typically, a crystalline material yields a spectrum with very sharp and intense Raman peaks, while an amorphous material shows broader and less intense Raman peaks.

The Raman spectra of PPy thin film shows **Figure 4**, The most important peak at about 1589 cm^{-1} which can be attributed to the C=C backbone stretching of PPy. The peak at about 1052 cm^{-1} is assigned to the C-H in plane deformation. Another peak at 1393 cm^{-1} is attributed to the ring-stretching mode of PPy. The band located at about 925 and 988 cm^{-1} are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively¹⁸⁻²⁰.

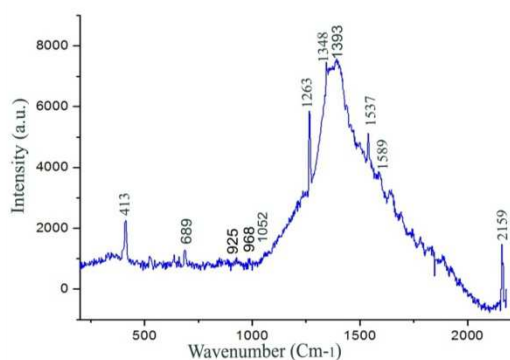


Figure 4 Raman scattering spectra of PPy Thin film

3.5. UV – Vis Spectroscopy Analysis

The UV- Vis spectroscopy of polypyrrole thin film is shown in the **Figure 5**. These absorption spectra have been recorded over wavelength range 300 to 1100 nm using a Lambda 35 UV-Vis spectroscopy model at room temperature two main absorption bands are present in this region for 469 and 590 nm. The film displayed strong absorption peak at 469nm, assigned as transitions from the PPy valance band to an anti-bipolarons band. This broad absorption is attributed to electron transition from the polypyrrole valence band to a second bipolarons band in the band gap^{21, 22}.

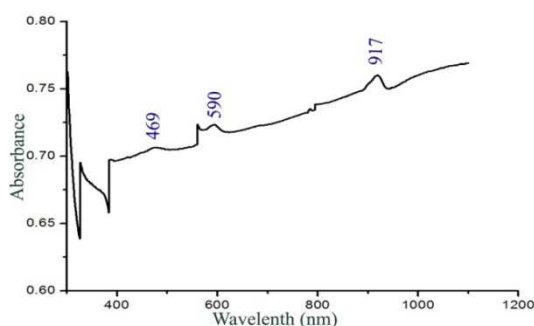


Figure 5 UV-Vis absorbance spectrum of PPy Thin film

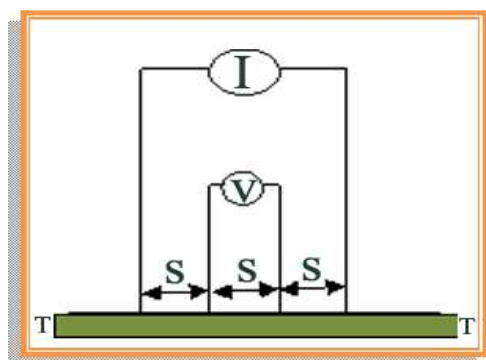


Figure 6: Four-point probe resistance measurement technique

3.6. Conductivity study

Thin films of PPy sample were measured for resistance using four-point probe technique show in **Figure 6**.

The four probe technique is a very efficient method for measuring the sheet resistance^{23,24}. It measures the sample resistance by current that flows for a given applied voltage. The outer two pins force a current through the sample and the inner two pins measure the voltage drop. The resistance of the pure PPy Spin Coated Thin film variation of electrical resistance as a function of temperature²⁵. In this case it was observed that as temperature increases the electrical resistance decreases and hence conductivity increases so in this film suggests that the thermally activated behaviour of conductivity has been confirmed.

4. CONCLUSIONS

The Polypyrrole synthesized using chemical polymerization process and thin film coated with Spin coating technique. The film non uniform distribution of particles morphology and structure of PPy confirmed by FTIR, XRD and Raman Spectroscopy techniques. UV-Vis studies showed that the PPy films exhibit absorption peak at 469 nm. The pure PPy thin film shows a thermally activated of conductivity.

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